THE INVERSE KINETIC ENERGY MATRIX ELEMENTS FOR THE OUT-OF-PLANE VIBRATIONS IN FURAN THIOPHENE, CYCLOPENTADIENE AND THEIR SUBSTITUTED COMPOUNDS

V. SANTHAMMA

DEPARTMENT OF PHYSICS, ANDHRA UNIVERSITY, WALTAIR

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ABSTRACT. The inverse kinetic energy matrix elements for the torsional vibrations, out-of-plane bending vibrations and the interaction between the above two are derived for furan, pyrrole, thiophene, and cyclopentadiene using the vector expressions given by Malhiot and Ferigle (1955). The applicability of these expressions to the substituted compounds of the above parent molecules and the limitations imposed are discussed.

INTRODUCTION

In the process of computing the vibrational frequencies of polyatomic molecules using the well-known Wilson's $F-G$ matrix method the calculation of the inverse kinetic energy matrix elements is the most important step. The inverse kinetic energy matrix element is defined for a pair of internal coordinates k and k' by Wilson (1939, 1941) as

$$g_{KK'} = \sum_{t=1}^{N} \mu_t \, \vec{s}_{kt} \cdot \vec{s}_{k't} \qquad \ldots \quad (1)$$

where $\vec{s}_{kt}$ is a vector representing the contribution of the t^{th} atom. The summation is done over all the atoms. This matrix is transformed into another matrix (G) by means of a transformation matrix U and its transpose U', the details and the application of which are given already elsewhere. (Santhamma, 1954).

Decius (1948) gave general formulae for the inverse kinetic energy matrix elements in terms of three types of internal coordinates* only. He considered 33 possible acyclic configurations in which case, the distinct types of configurations were specified following a definite notation (Decius, 1948) for the acyclic configuration of atoms defining super-positions of coordinates k and k'.

Malhiot and Ferigle (M and F, 1954), while discussing the consistency of Wilson's treatment with the Eckart conditions in the molecular vibrations, arrived at two important relations with regard to these $\vec{s}_{kt}$ vectors, namely

$$\sum_{t} \vec{s}_{kt} = 0 \qquad \ldots \quad (2)$$

* Bond stretching, inter-bond bending and torsion coordinates.

$$\Sigma \vec{r_t^0} \times \vec{s_{kt}} = 0 \quad \ldots (3)$$

where $\vec{r_t^0}$ is the equilibrium position vector of the t^{th} atom with respect to the centre of mass of the molecule. These two relations together with the gradient properties of $\vec{s_{kt}}$ vectors led to expressions of the vectors for all the four types of internal coordinates (Decius, 1949) of vibrations of polyatomic molecules. The vector expressions for the end atoms defining the torsion coordinate are the same as derived by Decius (1948) and all the four for the out-of-plane bending coordinate are same as given by Lohman (1951).

The purpose of the present paper is

(a) to derive vector expressions for another important class of molecules furan, pyrrole, thiophene and cyclopentadiene when torsion and out-of-plane bending coordinates are considered using the notation and expressions of Malhiot and Ferigle (1955), (b) to compute inverse kinetic energy matrix *elements* $g_{kk'}$ with the help of the expressions given in (a) and equation (1) and (c) to discuss the applicability of the expressions given in (a) and (b) for the substituted furans, pyrroles, thiophenes and cyclopentadienes and the limitations imposed.

(a) *Vector Expressions*

1. *General case of five membered ring compound*

At first a general case of a pentacyclic compound is taken where the angles and bond lengths in the equilibrium position are all different from one another, atoms of the ring are numbered from 1 to 5 consecutively around the ring in the cyclic manner shown in figure 1, a, b, c, d, e in this figure indicate atoms.

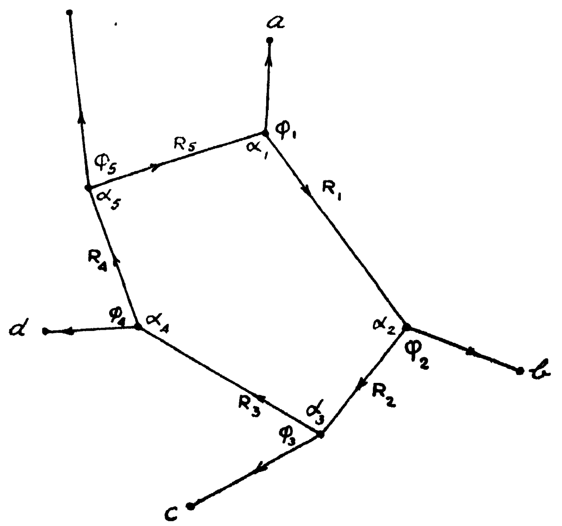

Fig. 1

The equilibrium angles, distances and the direction of the unit vectors along the bonds are indicated in the figure 1. The five torsion coordinates are designated by

$$\tau_{12}^{53},\ \tau_{23}^{14},\ \tau_{34}^{25},\ \tau_{45}^{31} \text{ and } \tau_{51}^{42}.$$

following the notation of M and F, but these are here simply written as τ_1, τ_2, τ_3, τ_4 and τ_5. The complete set of vector expressions in this case are presented in Table I.

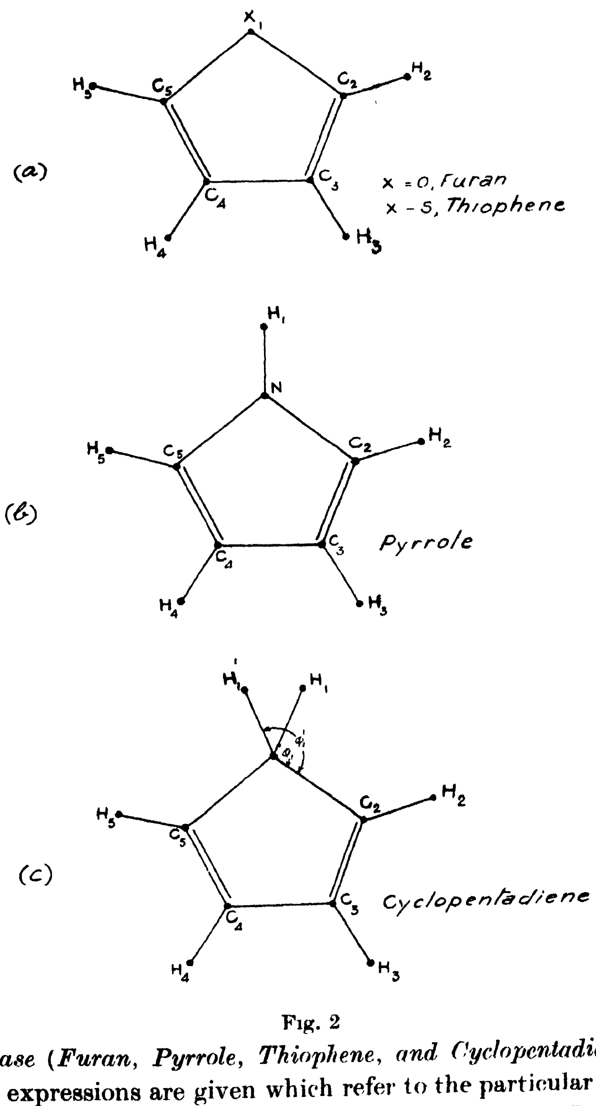

Fig. 2

2. *Particular case (Furan, Pyrrole, Thiophene, and Cyclopentadiene).*

In Table II expressions are given which refer to the particular case of furan, thiophene, pyrrole and cyclopentadiene (ref. Fig. 2). In these R_1, R_2, R_3 stand for the equilibrium distances of C—X (where X stands for O, S, NH or CH_2) C = C and C—C respectively.

TABLE I

Atoms of the ring / Coordinates	τ^{53}_{12}, τ_1	τ^{14}_{23}, τ_2	τ^{25}_{34}, τ_3	τ^{31}_{45}, τ_4	τ^{42}_{51}, τ_5
1	$-\vec{V}\left[\frac{1}{R_5}\text{cosec}\,\alpha_1-\frac{1}{R_1}(\cot\alpha_1+\cot\alpha_2)\right]$	$\frac{\vec{V}}{R_1}\text{cosec}\,\alpha_2$		$-\frac{\vec{V}}{R_5}\text{cosec}\,\alpha_5$	$\vec{V}\left[\frac{1}{R_1}\text{cosec}\,\alpha_1-\frac{1}{R_5}(\cot\alpha_1+\cot\alpha_5)\right]$
2	$\vec{V}\left[\frac{1}{R_2}\text{cosec}\,\alpha_2-\frac{1}{R_1}(\cot\alpha_1+\cot\alpha_2)\right]$	$-\vec{V}\left[\frac{1}{R_1}\text{cosec}\,\alpha_2-\frac{1}{R_2}(\cot\alpha_2+\cot\alpha_3)\right]$	$\frac{\vec{V}}{R_2}\text{cosec}\,\alpha_3$		$-\frac{\vec{V}}{R_1}\text{cosec}\,\alpha_1$
3	$-\frac{\vec{V}}{R_2}\text{cosec}\,\alpha_2$	$\vec{V}\left[\frac{1}{R_3}\text{cosec}\,\alpha_3-\frac{1}{R_2}(\cot\alpha_2+\cot\alpha_3)\right]$	$-\vec{V}\left[\frac{1}{R_2}\text{cosec}\,\alpha_3-\frac{1}{R_3}(\cot\alpha_3+\cot\alpha_4)\right]$	$\frac{\vec{V}}{R_3}\text{cosec}\,\alpha_3$	
4		$-\frac{\vec{V}}{R_3}\text{cosec}\,\alpha_3$	$\vec{V}\left[\frac{1}{R_4}\text{cosec}\,\alpha_4-\frac{1}{R_3}(\cot\alpha_3+\cot\alpha_4)\right]$	$-\vec{V}\left[\frac{1}{R_3}\text{cosec}\,\alpha_3-\frac{1}{R_4}(\cot\alpha_4+\cot\alpha_5)\right]$	$\frac{\vec{V}}{R_4}\text{cosec}\,\alpha_5$
5	$\frac{\vec{V}}{R_5}\text{cosec}\,\alpha_1$		$-\frac{\vec{V}}{R_4}\text{cosec}\,\alpha_4$	$\vec{V}\left[\frac{1}{R_5}\text{cosec}\,\alpha_5-\frac{1}{R_4}(\cot\alpha_4+\cot\alpha_5)\right]$	$-\vec{V}\left[\frac{1}{R_4}\text{cosec}\,\alpha_5-\frac{1}{R_5}(\cot\alpha_1+\cot\alpha_5)\right]$

TABLE II

Atmos of the ring \ Co-ordinates	τ_1	τ_2	τ_3	τ_4	τ_5
C_1, O, S, N	$-\frac{\vec{V}}{R_1}\left[\text{cosec}\,\delta_1+\cot\delta_1+\cot\delta_2\right]$	$\frac{\vec{V}}{R_1}\text{cosec}\,\delta_2$		$-\frac{\vec{V}}{R_1}\text{cosec}\,\delta_2$	$\frac{\vec{V}}{R_1}\left[\text{cosec}\,\delta_1+\cot\delta_1+\cot\delta_2\right]$
C_2	$\vec{V}\left[\frac{1}{R_2}\text{cosec}\,\delta_2+\frac{1}{R_1}(\cot\delta_2+\cot\delta_1)\right]$	$-\vec{V}\left[\frac{1}{R_1}\text{cosec}\,\delta_2+\frac{1}{R_2}(\cot\delta_2+\cot\delta_3)\right]$	$\frac{\vec{V}}{R_2}\text{cosec}\,\delta_3$		$-\frac{\vec{V}}{R_1}\text{cosec}\,\delta_1$
C_3	$-\frac{\vec{V}}{R_2}\text{cosec}\,\delta_2$	$\vec{V}\left[\frac{1}{R_3}\text{cosec}\,\delta_3+\frac{1}{R_2}(\cot\delta_2+\cot\delta_3)\right]$	$-\vec{V}\left[\frac{1}{R_2}\text{cosec}\,\delta_3+\frac{2}{R_3}\cot\delta_3\right]$	$\frac{\vec{V}}{R_3}\text{cosec}\,\delta_3$	
C_4		$-\frac{\vec{V}}{R_3}\text{cosec}\,\delta_3$	$\vec{V}\left[\frac{1}{R_2}\text{cosec}\,\delta_3+\frac{2}{R_3}\cot\delta_3\right]$	$-\vec{V}\left[\frac{1}{R_3}\text{cosec}\,\delta_3+\frac{1}{R_2}(\cot\delta_2+\cot\delta_3)\right]$	$\frac{\vec{V}}{R_2}\text{cosec}\,\delta_2$
C_5	$\frac{\vec{V}}{R_1}\text{cosec}\,\delta_1$		$-\frac{\vec{V}}{R_2}\text{cosec}\,\delta_3$	$\vec{V}\left[\frac{1}{R_1}\text{cosec}\,\delta_2+\frac{1}{R_2}(\cot\delta_2+\cot\delta_3)\right]$	$-\vec{V}\left[\frac{1}{R_2}\text{cosec}\,\delta_2+\frac{1}{R_1}(\cot\delta_2+\cot\delta_1)\right]$

TABLE III

Atoms of the ring / Co-ordinates	$\gamma^{a}_{512}, \gamma_1$	$\gamma^{b}_{123}, \gamma_2$	$\gamma^{c}_{234}, \gamma_3$	$\gamma^{d}_{345}, \gamma_4$	$\gamma^{e}_{451}, \gamma_5$
a	$-\frac{\vec{V}}{r_1}\sin\varphi_1 \operatorname{cosec}\alpha_1$				
b		$-\frac{\vec{V}}{r_2}$ s n $\varphi_2 \operatorname{cosec}\alpha_2$			
c			$-\frac{\vec{V}}{r_3}\sin\varphi_3 \operatorname{cosec}\alpha_3$		
d				$-\frac{\vec{V}}{r_4}\sin\varphi_4 \operatorname{cosec}\alpha_4$	
e					$-\frac{\vec{V}}{r_5}\sin\varphi_5 \operatorname{cosec}\alpha_5$
1	$\vec{V}\sin\varphi_1 \operatorname{cosec}^3\alpha_1$ $\left[\frac{1}{r_1}\text{s in}^2\alpha_1+\frac{1}{R_5}\sin\phi_1 \sin\alpha_1+\frac{1}{R_1}(\cos\alpha_1\cos\beta_1 -\cos\varphi_1)\right]$	$-\frac{\vec{V}}{R_1}\sin{}^2\varphi_2 \operatorname{cosec}{}^2\alpha_2$			$-\frac{\vec{V}}{R_5}\sin\varphi_5 \operatorname{cosec}{}^3\alpha_5$ $(\cos\alpha_5\cos\beta_5\cos\phi_5)$
2	$-\frac{\vec{V}}{R_1}\sin\varphi_1 \operatorname{cosec}^3\alpha_1$ $(\cos\alpha_1\cos\beta_1-\cos\phi_1)$	$\vec{V}\sin\varphi_2 \operatorname{cosec}{}^3\alpha_2$ $\left[\frac{1}{r_2}\sin^2\alpha_2+\frac{1}{R_1}\sin\varphi_2 \sin\alpha_2+\frac{1}{R_2}(\cos\alpha_2 \cos\beta_2-\cos\varphi_2)\right]$	$-\frac{\vec{V}}{R_2}\sin{}^2\varphi_3 \operatorname{cosec}{}^2\alpha_3$		

TABLE III (*contd.*)

Atoms of the ring | Co-ordinates	γ^a_{511},γ_1	γ^b_{103},γ_0	γ^c_{034},γ_3	γ^d_{345},γ_4	$\gamma^e_{451}\gamma_5$
3		$-\frac{\vec{V}}{R_2}\sin\varphi_2 \operatorname{cosec}^3\alpha_2$ $(\cos\alpha_2 \cos\beta_2-\cos\varphi_2)$	$\vec{V}\sin\varphi_3 \operatorname{cosec}^3\alpha_3$ $\left[\frac{1}{r_3}\sin^2\alpha_3 + \frac{1}{R_2}\sin\varphi_3 \sin\alpha_3 + \frac{1}{R_3}\right.$ $\left.(\cos\alpha_3 \cos\beta_3 - \cos\varphi_3)\right]$	$-\frac{\vec{V}}{R_3}\sin^2\phi_4 \operatorname{cosec}^2\alpha_4$	
4			$-\frac{\vec{V}}{R_3}\sin\varphi_3 \operatorname{cosec}^3\alpha_3$ $(\cos\alpha_3 \cos\beta_3-\cos\phi_3)$	$\vec{V}\sin\varphi_4 \operatorname{cosec}^3\alpha_4$ $\left[\frac{1}{r_4}\sin^2\alpha_4 + \frac{1}{R_3}\sin\varphi_4 \sin\alpha_4\right.$ $\left.+\frac{1}{R_4}(\cos\alpha_4\cos\beta_4-\cos\varphi_4)\right]$	$-\frac{\vec{V}}{R_4}\sin^2\varphi_4 \operatorname{cosec}^2\alpha_4$
5	$-\frac{\vec{V}}{R_5}\sin^2\phi_1 \operatorname{cosec}^2\alpha_1$			$-\frac{\vec{V}}{R_4}\sin\varphi_4 \operatorname{cosec}^3\alpha_4$ $(\cos\alpha_4 \cos\beta_4-\cos\varphi_4)$	$\vec{V}\sin\varphi_5 \operatorname{cosec}^3\alpha_5$ $\left[\frac{1}{r_5}\sin^2\alpha_5 + \frac{1}{R_4}\sin\varphi_5 \sin\alpha_5\right.$ $\left.+\frac{1}{R_5}(\cos\alpha_5\cos\beta_5-\cos\varphi_5)\right]$

$\beta_i = 360-(\varphi_i+\alpha_i)$

TABLE IV

Atoms of the molecule \ co-ordinates	H_1 γ_{512},γ_1	H_2 γ_{123},γ_2	H_3 γ_{234},γ_3	H_4 γ_{345},γ_4	H_5 γ_{451},γ_5	H'_1 γ_{512},γ'_1
H_1	$-\frac{\vec{V}}{r_1}\sin\varphi_1\,\mathrm{cosec}\,\alpha_1$					
H_2		$-\frac{\vec{V}}{r_2}\sin\varphi_2\,\mathrm{cosec}\,\alpha_2$				
H_3			$-\frac{\vec{V}}{r_3}\sin\varphi_3\,\mathrm{cosec}\,\alpha_3$			
H_4				$-\frac{\vec{V}}{r_4}\sin\varphi_3\,\mathrm{cosec}\,\alpha_3$		
H_5					$-\frac{\vec{V}}{r_5}\sin\varphi_2\,\mathrm{cosec}\,\alpha_2$	
H_1						$-\frac{\vec{V}}{r'_1}\sin\varphi'_1\,\mathrm{cosec}\,\alpha_1$
C_1, S, O, N	$\vec{V}\sin\varphi_1\,\mathrm{cosec}^3\alpha_1\left[\frac{1}{r_1}\sin^2\alpha_1 + \frac{2}{R_1}\sin\alpha_1\sin\varphi_1\right]$	$-\frac{\vec{V}}{R_1}\sin^2\varphi_2\,\mathrm{cosec}^2\alpha_2$			$-\frac{\vec{V}}{R_1}\sin^2\varphi_2\,\mathrm{cosec}^2\alpha_2$	$\vec{V}\sin\varphi'_1\,\mathrm{cosec}^3\alpha_1\left[\frac{1}{r'_1}\sin^2\alpha_1 \quad \frac{2}{R_1}\sin\varphi'_1\sin\alpha_1\right]$
C_2	$-\frac{\vec{V}}{R_1}\sin^2\varphi_1\,\mathrm{cosec}^2\alpha_1$	$\vec{V}\sin\varphi_2\,\mathrm{cosec}^3\alpha_2\left[\frac{1}{r_2}\sin^2\alpha_2 + \left(\frac{1}{R_1}+\frac{1}{R_2}\right)\sin\alpha_2\sin\varphi_2\right]$	$-\frac{\vec{V}}{R_2}\sin^2\varphi_3\,\mathrm{cosec}^2\alpha_3$			$-\frac{\vec{V}}{R_1}\sin^2\varphi'_3\,\mathrm{cosec}^2\alpha_1$

TABLE IV (*contd.*)

Atoms of the molecule / co-ordinates.	H_1 γ_{512}, γ_1	H_2 γ_{123}, γ_2	H_3 γ_{234}, γ_3	H_4 γ_{345}, σ_4	H_5 γ_{451}, γ_5	H'_1 γ_{512}, γ'_1
C_3		$-\frac{\vec{V}}{R_3}\sin^2\varphi_2 \operatorname{cosec}^2\alpha_2$	$\vec{V}\sin\varphi_3 \operatorname{cosec}^3\alpha_3 \left[\frac{1}{r_3}\sin^2\alpha_3 + \left(\frac{1}{R_2}+\frac{1}{R_3}\right)\sin\varphi_3 \sin\alpha_3\right]$	$-\frac{\vec{V}}{R_3}\sin^2\varphi_3 \operatorname{cosec}^2\alpha_3$		
C_4			$-\frac{\vec{V}}{R_3}\sin^2\varphi_3 \operatorname{cosec}^2\alpha_3$	$\vec{V}\sin\varphi_3 \operatorname{cosec}^3\alpha_3 \left[\frac{1}{r_4}\sin^2\alpha_3 - \left(\frac{1}{R_3}+\frac{1}{R_2}\right)\sin\varphi_3 \sin\alpha_3\right]$	$-\frac{\vec{V}}{R_2}\sin^2\varphi_2 \operatorname{cosec}^2\alpha_2$	
C_5	$-\frac{\vec{V}}{R_1}\sin^2\varphi_1 \operatorname{cosec}^2\alpha_1$			$-\frac{\vec{V}}{R_2}\sin^2\varphi_3 \operatorname{cosec}^2\alpha_3$	$\vec{V}\sin\varphi_2 \operatorname{cosec}^3\alpha_2 \left[\frac{1}{r_5}\sin^2\alpha_2 + \left(\frac{1}{R_2}+\frac{1}{R_1}\right)\sin\varphi_2 \sin\alpha_2\right]$	$-\frac{\vec{V}}{R_1}\sin^2\varphi'_1 \operatorname{cosec}^2\alpha_1$

TABLE A

Coordinates k k'	μ_X	μ_C
$\left.\begin{matrix}\tau_1 & \tau_1 \\ \tau_5 & \tau_5\end{matrix}\right\}$	$\frac{1}{R_1^2}(\operatorname{cosec}\delta_1+\cot\delta_1+\cot\delta_2)^2$	$\left[\left\{\frac{1}{R_2}\operatorname{cosec}\delta_2+\frac{1}{R_1}(\cot\delta_2+\cot\delta_1)\right\}^2+\frac{1}{R_2^2}\operatorname{cosec}^2\delta_2+\frac{1}{R_1^2}\operatorname{csec}^2\delta_1\right]$
$\left.\begin{matrix}\tau_2 & \tau_2 \\ \tau_4 & \tau_4\end{matrix}\right\}$	$\frac{1}{R_1^2}\operatorname{cosec}^2\delta_2$	$\left[\left\{\frac{1}{R_1}\operatorname{cosec}\delta_2+\frac{1}{R_2}(\cot\delta_2+\cot\delta_3)\right\}^2-\frac{1}{R_3^2}\operatorname{cosec}^2\delta_3-\left\{\frac{1}{R_3}\operatorname{cosec}\delta_3+\frac{1}{R_2}(\cot\delta_2-\cot\delta_3)\right\}^2\right]$
τ_3 τ_3		$2\left[\frac{1}{R_2^2}\operatorname{cosec}^2\delta_3+\left(\frac{1}{R_2}\operatorname{cosec}\delta_3-\frac{2}{R_3}\cot\delta_3\right)^2\right]$
$\left.\begin{matrix}\tau_1 & \tau_2 \\ \tau_4 & \tau_5\end{matrix}\right\}$	$-\frac{1}{R_1^2}\operatorname{cosec}\delta_2(\operatorname{cosec}\delta_1+\cot\delta_1+\cot\delta_2)$	$-\left[\left\{\frac{1}{R_2}\operatorname{cosec}\delta_2+\frac{1}{R_1}(\cot\delta_2+\cot\delta_1)\right\}\left\{\frac{1}{R_1}\operatorname{cosec}\delta_2+\frac{1}{R_2}(\cot\delta_2+\cot\delta_3)\right\}+\frac{1}{R_2}\operatorname{cosec}\delta_2\left\{\frac{1}{R_3}\operatorname{cosec}\delta_3+\frac{1}{R_2}(\cot\delta_2+\cot\delta_3)\right\}\right]$
τ_2 τ_3		$\left[\frac{1}{R_2}\operatorname{cosec}\delta_3\left\{\frac{1}{R_2}\operatorname{cosec}\delta_2+\frac{1}{R_1}(\cot\delta_2+\cot\delta_1)\right\}+\frac{1}{R_2}\operatorname{cosec}\delta_2\left\{\frac{1}{R_2}\operatorname{cosec}\delta_3+\frac{2}{R_3}\cot\delta_3\right\}-\frac{1}{R_1R_2}\operatorname{cosec}\delta_1\operatorname{cosec}\delta_3\right]$
τ_1 τ_4	$\frac{1}{R_1^2}\operatorname{cosec}\delta_2(\operatorname{cosec}\delta_1+\cot\delta_1+\cot\delta_2)$	$\left[-\frac{1}{R_2R_3}\operatorname{cosec}\delta_2\operatorname{cosec}\delta_3+\frac{1}{R_1}\operatorname{cosec}\delta_1\left\{\frac{1}{R_1}\operatorname{cosec}\delta_2+\frac{1}{R_2}(\cot\delta_2+\cot\delta_3)\right\}\right]$

TABLE A (*contd*)

Coordinates k k'	μ_X	μ_C
τ_1 τ_5	$-\frac{1}{R_1^2}(\text{cosec}\ \delta_1+\cot\delta_1+\cot\delta_2)^2$	$\left[-\frac{2}{R_1}\text{cosec}\ \delta_1\left\{\frac{1}{R_2}\text{cosec}\ \delta_2+\frac{1}{R_1}(\cot\delta_1+\cot\delta_2)\right\}\right]$
τ_2 τ_3		—
τ_3 τ_4		$-\left[\frac{1}{R_2}\text{cosec}\ \delta_3\left\{\frac{1}{R_1}\text{cosec}\ \delta_2-\frac{1}{R_2}(\cot\delta_2+\cot\delta_3)\right\}+\left\{\frac{1}{R_3}\text{cosec}\ \delta_3+\frac{1}{R_2}(\cot\delta_2+\cot\delta_3)\right\}\left\{\frac{1}{R_2}\text{cosec}\ \delta_3+\frac{2}{R_3}\cot\delta_3\right\}+\frac{1}{R_3}\text{cosec}\ \delta_3\left(\frac{1}{R_2}\text{cosec}\ \delta_3-\frac{2}{R_3}\cot\delta_3\right)\right]$
τ_2 τ_4	$-\frac{1}{R_1^2}\text{cosec}^2\ \delta_2$	$\left[\frac{2}{R_3}\text{cosec}\ \delta_3\left\{\frac{1}{R_3}\text{cosec}\ \delta_3+\frac{1}{R_2}(\cot\delta_2+\cot\delta_3)\right\}\right]$
τ_2 τ_6	$\frac{1}{R_1^2}\text{cosec}\ \delta_2(\text{cosec}\ \delta_1-\cot\delta_1+\cot\delta_2)$	$\left[\frac{1}{R_1}\text{cosec}\ \delta_1\left\{\frac{1}{R_1}\text{cosec}\ \delta_2-\frac{1}{R_2}(\cot\delta_2-\cot\delta_3)\right\}-\frac{1}{R_2R_3}\text{cosec}\ \delta_2\ \text{cosec}\ \delta_3\right]$
τ_3 τ_5		$\left[-\frac{1}{R_1R_2}\text{cosec}\ \delta_1\ \text{cosec}\ \delta_3-\frac{1}{R_2}\text{cosec}\ \delta_2\left(\frac{1}{R_2}\text{cosec}\ \delta_3+\frac{2}{R_3}\cot\delta_3\right)+\frac{1}{R_2}\text{cosec}\ \delta_3\left\{\frac{1}{R_2}\text{cosec}\ \delta_2-\frac{1}{R_1}(\cot\delta_2+\cot\delta_1)\right\}\right]$
	$g_{kk'}=g_{k'k}$	

TABLE B

Coordinate k	k'	μ_H	μ_X	μ_C
γ_1	γ_1	$\frac{1}{r_1^2}\sin^2\varphi_1 \operatorname{cosec}^2\alpha_1$	$\sin^2\varphi_1 \operatorname{cosec}^6\alpha_1\left(\frac{1}{r_1}\sin^2\alpha_1-\frac{2}{R_1}\sin\alpha_1\sin\varphi_1\right)^2$	$\frac{2}{R_1^2}\sin^4\varphi_1 \operatorname{cosec}^2\alpha_1$
γ_1'	γ_1'	$\frac{1}{r_1'^2}\sin^2\varphi'_1 \operatorname{cosec}^2\alpha_1$	$\sin^2\varphi_1' \operatorname{cosec}^6\alpha_1\left(\frac{1}{r_1'}\sin^2\alpha_1-\frac{2}{R_1}\sin\varphi'_1\sin\alpha_1\right)^2$	$\frac{2}{R_1^2}\sin^4\varphi_1' \operatorname{cosec}^4\alpha_1$
γ_2 γ_5	$\left.\begin{matrix}\gamma_2\\ \gamma_5\end{matrix}\right\}$	$\frac{1}{r_{2,5}^2}\sin^2\varphi_2 \operatorname{cosec}^2\alpha_2$	$\frac{1}{R_1^2}\sin^4\varphi_2 \operatorname{cosec}^4\alpha_2$	$\left[\frac{1}{R_2^2}\sin^4\varphi_2 \operatorname{cosec}^4\alpha_2+\sin^2\varphi_2 \operatorname{cosec}^6\alpha_2\left\{\frac{1}{r_{2,5}}\sin^2\alpha_2+\left(\frac{1}{R_1}+\frac{1}{R_2}\right)\sin\alpha_2\sin\varphi_2\right\}^2\right]$
γ_3 γ_4	$\left.\begin{matrix}\gamma_3\\ \gamma_4\end{matrix}\right\}$	$\frac{1}{r_{3,4}}\sin^2\varphi_3 \operatorname{cosec}^2\alpha_3$		$\left[\left(\frac{1}{R_2^2}+\frac{1}{R_3^2}\right)\sin^4\varphi_3 \operatorname{cosec}^4\alpha_3+\sin^2\varphi_3 \operatorname{cosec}^6\alpha_3\left\{\frac{1}{r_{3,4}}\sin^2\alpha_3+\left(\frac{1}{R_2}+\frac{1}{R_3}\right)\sin\varphi_3\sin\alpha_3\right\}^2\right]$
γ_1 γ_1	$\left.\begin{matrix}\gamma_2\\ \gamma_5\end{matrix}\right\}$		$-\left(\frac{1}{R_1}\sin^2\varphi_2 \operatorname{cosec}^2\alpha_2\sin\varphi_1 \operatorname{cosec}^3\alpha_1\right)\left(\frac{1}{r_1}\sin^2\alpha_1+\frac{2}{R_1}\sin\alpha_1\sin\varphi_3\right)$	$\left[-\left(\frac{1}{R_1}\sin^2\varphi_1 \operatorname{cosec}^2\alpha_1\sin\varphi_2 \operatorname{cosec}^3\alpha_2\right)\left(\frac{1}{r_{2,5}}\sin^2\alpha_2+\left(\frac{1}{R_1}+\frac{1}{R_2}\right)\sin\alpha_2\sin\varphi_2\right)\right]$
				$\frac{1}{R_1R_2}\sin^2\varphi_1\sin^2\varphi_3 \operatorname{cosec}^2\alpha_1 \operatorname{cosec}^2\alpha_3$
γ_1 γ_1	$\left.\begin{matrix}\gamma_3\\ \gamma_4\end{matrix}\right\}$			$\left[-\left(\frac{1}{R_2}\sin^2\varphi_3 \operatorname{cosec}^3\alpha_3\sin\varphi_2 \operatorname{cosec}^3\alpha_2\right)\right.$
γ_2 γ_4	$\left.\begin{matrix}\gamma_3\\ \gamma_5\end{matrix}\right\}$			$\left\{\frac{1}{r_{2,5}}\sin^2\alpha_2+\left(\frac{1}{R_1}+\frac{1}{R_2}\right)\sin\alpha_2\sin\varphi_2\right\}$ $-\left(\frac{1}{R_2}\sin^2\varphi_2 \operatorname{cosec}^2\alpha_2\sin\varphi_3 \operatorname{cosec}^3\alpha_3\right)$

TABLE B (contd.)

Coordinates k	k'	μ_H	μ_X	μ_C
				$\left\{ \frac{1}{r_{3,4}} \sin^2\alpha_3 - \left(\frac{1}{R_2} + \frac{1}{R_3} \right) \sin\varphi_3 \sin\alpha_3 \right\} \Big]$
γ_2 γ_3	$\left.\begin{matrix}\gamma_4 \\ \gamma_5\end{matrix}\right\}$			$\frac{1}{R_2R_3} \sin^2\varphi_2 \sin^2\varphi_3 \operatorname{cosec}^2\alpha_2 \operatorname{cosec}^2\alpha_3$
γ_2	γ_5		$\frac{1}{R_1^2} \sin^4\varphi_2 \operatorname{cosec}^4\alpha_2$	
γ_3	γ_4			$\Big[-\frac{1}{R_3} \sin^3\varphi_3 \operatorname{cosec}^5\alpha_3 \left\{ \frac{1}{r} \sin^2\alpha_3 + \frac{1}{r_4} \sin^2\alpha_3 \right.$ $2\left(\frac{1}{R_2} + \frac{1}{R_3}\right) \sin\varphi_3 \sin\alpha_3$)
γ_2 γ_5	$\left.\begin{matrix}\gamma_1' \\ \gamma_1'\end{matrix}\right\}$		$\Big[-\left(\frac{1}{R_1} \sin^2\varphi_2 \sin\varphi_1' \operatorname{cosec}^2\alpha_2 \operatorname{cosec}^3\alpha_1\right)$ $\left(\frac{1}{r_1} \sin^2\alpha_1 + \frac{2}{R_1} \sin\varphi_1' \sin\alpha_1\right)\Big]$	$\Big[-\left(\frac{1}{R_1} \sin^2\varphi_1' \sin\varphi_2 \operatorname{cosec}^2\alpha_1 \operatorname{cosec}^3\alpha_2\right)$ $\left(\frac{1}{r_{2,5}} \sin^2\alpha_2 + \left(\frac{1}{R_1} - \frac{1}{R_2}\right) \sin\alpha_2 \sin\varphi_2 \right\} \Big]$
γ_1	γ_1'		$\Big[(\sin\varphi_1 \sin\varphi_1' \operatorname{cosec}^6\alpha_1)$ $\left(\frac{1}{r_1} \sin^2\alpha_1 - \frac{2}{R_1} \sin\alpha_1 \sin\varphi_1\right)$ $\left(\frac{1}{r'_1} \sin^2\alpha_1 + \frac{2}{R_1} \sin\varphi_1' \sin\alpha_1\right)\Big]$	$\Big[\frac{2}{R_1^2} \sin^2\varphi_1 \sin^2\varphi_1' \sin^4\alpha_1 \Big]$
γ_3 γ_4	γ_1' γ_1'			$\frac{1}{R_1R_2} \sin^2\varphi_3 \sin^2\varphi_1' \operatorname{cosec}^2\alpha_3 \operatorname{cosec}^2\alpha_1$

The first suffix with regards to r is to be associated always with the first pair of coordinates in the brackets under the first column . The same notation follows for the second suffix also.

TABLE C

Coordinates k	k'	μ_X	μ_C
τ_1	γ_1	$-\left\{\frac{1}{R_1}\sin\varphi_1 \operatorname{cosec}^3\alpha_1 (\operatorname{cosec}\delta_1 + \cot\delta_1 + \cot\delta_2)\right.$	$-\left[\frac{1}{R_1}\sin^2\varphi_1 \operatorname{cosec}^2\alpha_1 \left\{\frac{1}{R_2}\operatorname{cosec}\delta_2 + \frac{1}{R_1}(\cot\delta_2 + \cot\delta_1)\right\}\right.$
		$\left.\left(\frac{1}{r_1}\sin^2\alpha_1 + \frac{2}{R_1}\sin\alpha_1 \sin\varphi_1\right)\right\}$	$\left. + \frac{1}{R_1^2}\sin^2\varphi_1 \operatorname{cosec}^2\alpha_1 \operatorname{cosec}\delta_1\right]$
τ_2	γ_2	$-\frac{1}{R_1^2}\sin^2\varphi_2 \operatorname{cosec}^2\alpha_2 \operatorname{cosec}\delta_2$	$-\left[\sin\varphi_2 \operatorname{cosec}^3\alpha_2 \left\{\frac{1}{R_1}\operatorname{cosec}\delta_2 + \frac{1}{R_2}(\cot\delta_2 + \cot\delta_3)\right.\right.$
			$\left\{\frac{1}{r_2}\sin^2\alpha_2 + \left(\frac{1}{R_1} + \frac{1}{R_2}\right)\sin\alpha_2 \sin\varphi_2\right\} + \frac{1}{R_2}\sin^2\varphi_2 \operatorname{cosec}^2\alpha_2$
			$\left.\left.\left\{\frac{1}{R_3}\operatorname{cosec}\delta_3 + \frac{1}{R_2}(\cot\delta_2 + \cot\delta_3)\right\}\right\}\right]$
τ_3	γ_3		$-\left[\frac{1}{R_2^2}\sin^2\varphi_3 \operatorname{cosec}^2\alpha_3 \operatorname{cosec}\delta_3 + \left(\frac{1}{R_2}\operatorname{cosec}\delta_3 + \frac{2}{R_3}\cot\delta_3\right)\right.$
			$\left\{\sin\varphi_3 \operatorname{cosec}^3\alpha_3\right\}\left\{\frac{1}{r_3}\sin^2\alpha_3 + \left(\frac{1}{R_2} + \frac{1}{R_3}\right)\sin\varphi_3 \sin\alpha_3\right\} +$
			$\left.\frac{1}{R_3}\sin^2\varphi_3 \operatorname{cosec}^2\alpha_3 \left(\frac{1}{R_2}\operatorname{cosec}\delta_3 + \frac{2}{R_3}\cot\delta_3\right)\right]$
τ_4	γ_4		$-\left[\frac{1}{R_3^2}\sin^2\varphi_3 \operatorname{cosec}^2\varphi_3 \operatorname{cosec}\delta_3 + \left\{\frac{1}{R_3}\operatorname{cosec}\delta_3 + \frac{1}{R_2}(\cot\delta_2 + \cot\delta_3\right\}\right.$
			$\sin\varphi_3 \operatorname{cosec}^3\alpha_3\left\{\frac{1}{r_4}\sin^2\alpha_3 + \left(\frac{1}{R_3} + \frac{1}{R_2}\right)\sin\varphi_3 \sin\alpha_3\right\} +$
			$\left.\frac{1}{R_2}\sin^2\varphi_3 \operatorname{cosec}^2\alpha_3 \left\{\frac{1}{R_1}\operatorname{cosec}\delta_2 + \frac{1}{R_2}(\cot\delta_2 + \cot\delta_3)\right\}\right]$

TABLE C (*contd*)

Coordinate k	k'	μ_X	μ_C
τ_5	γ_5	$-\frac{1}{R_1^2}\sin^2\varphi_2\,\mathrm{cosec}^2\alpha_2\,(\mathrm{cosec}\,\delta_1+\cot\delta_1+\cot\delta_2)$	$-\Big[\frac{1}{R^2_2}\sin^2\varphi_2\,\mathrm{cosec}^2\alpha_2\,\mathrm{cosec}\,\delta_2+\Big\{\frac{1}{R_2}\,\mathrm{cosec}\,\delta_2+\frac{1}{R_1}(\cot\delta_2+\cot\delta_1)\Big]$
			$\sin\varphi_2\,\mathrm{cosec}^3\alpha_2\Big\{\frac{1}{r_5}\sin^2\alpha_2+\Big(\frac{1}{R_2}+\frac{1}{R_1}\Big)\sin\varphi_2\sin\alpha_2\Big\}\Big]$
τ_1	γ_2	$\frac{1}{R^2_1}\sin^2\varphi_2\,\mathrm{cosec}^2\alpha_2\,(\mathrm{cosec}\,\delta_1+\cot\delta_1+\cot\delta_2)$	$\Big[\Big\{\frac{1}{R_2}\,\mathrm{cosec}\,\delta_2+\frac{1}{R_1}(\cot\delta_1+\cot\delta_2)\Big\}\Big\{\sin\varphi_2\,\mathrm{cosec}^3\alpha_2\Big\}$
			$\Big\{\frac{1}{r_2}\sin^2\alpha_2+\Big(\frac{1}{R_1}+\frac{1}{R_2}\Big)\sin\alpha_2\sin\varphi_2\Big\}+\frac{1}{R^2_2}\sin^2\varphi_2\,\mathrm{cosec}^2\alpha_2\,\mathrm{cosec}\,\delta_2\Big]$
τ_1	γ_3		$-\Big[\frac{1}{R_2}\sin^2\varphi_3\,\mathrm{cosec}^2\alpha_3\Big\{\frac{1}{R_2}\,\mathrm{cosec}\,\delta_2-\frac{1}{R_1}(\cot\delta_2+\cot\delta_1)\Big\}$
			$+\frac{1}{R_2}\sin\varphi_3\,\mathrm{cosec}^3\varphi_3\,\mathrm{cosec}\,\delta_2\Big\{\frac{1}{r_3}\sin^2\alpha_3+\Big(\frac{1}{R_2}+\frac{1}{R_3}\Big)\sin\varphi_3\sin\alpha_3\Big\}\Big]$
τ_1	γ_4		$\Big[\frac{1}{R_2R_3}\,\mathrm{cosec}\,\delta_2\,\mathrm{cosec}^2\alpha_3\sin^2\varphi_3-\frac{1}{R_1R_2}\,\mathrm{cosec}\,\delta_1\,\mathrm{cosec}^2\alpha_3\sin^2\varphi_3\Big]$
τ_1	γ_5	$\frac{1}{R_1^2}\sin^2\varphi_2\,\mathrm{cosec}^2\alpha_2\,(\mathrm{cosec}\,\delta_1+\cot\delta_1+\cot\delta_2)$	$\Big[\frac{1}{R_1}\sin\varphi_2\,\mathrm{cosec}^3\alpha_2\,\mathrm{cosec}\,\delta_1\Big\{\frac{1}{r_5}\sin^2\alpha_2+\Big(\frac{1}{R_2}+\frac{1}{R_1}\Big)\sin\varphi_2\sin\alpha_2\Big\}\Big]$
τ_2	γ_1	$\frac{1}{R_1}\sin\varphi_1\,\mathrm{cosec}^3\alpha_1\,\mathrm{cosec}\,\delta_2\Big(\frac{1}{r_1}\sin^2\alpha_1+\frac{2}{R_1}\sin\alpha_1\sin\varphi_1\Big)$	$\Big[\frac{1}{R_1}\sin^2\varphi_1\,\mathrm{cosec}^2\alpha_1\Big\{\frac{1}{R_1}\,\mathrm{cosec}\,\delta_2+\frac{1}{R_2}(\cot\delta_2+\cot\delta_3)\Big\}\Big]$
τ_2	γ_3		$\Big[\frac{1}{R_2}\sin^2\varphi_3\,\mathrm{cosec}^2\alpha_3\Big\{\frac{1}{R_1}\,\mathrm{cosec}\,\delta_2-\frac{1}{R_2}(\cot\delta_2+\cot\delta_3)\Big\}$
			$+\sin\varphi_3\,\mathrm{cosec}^3\alpha_3\Big\{\frac{1}{R_3}\,\mathrm{cosec}\,\delta_3+\frac{1}{R_2}(\cot\delta_2-\cot\delta_3)\Big\}$

TABLE C (*contd.*)

Coordinates k	k'	μ_X	μ_C
			$\left\{\frac{1}{r_3}\sin^2\alpha_3 - \left(\frac{1}{R_2}+\frac{1}{R_3}\right)\sin\varphi_3\sin\alpha_3\right\} - \frac{1}{R_3^2}\sin^2\varphi_3\,\mathrm{cosec}^2\alpha_3\,\mathrm{cosec}\,\delta_3\Big]$
τ_2	γ_4		$-\Big[\frac{1}{R_3}\sin^2\varphi_3\,\mathrm{cosec}^2\alpha_3\left\{\frac{1}{R_3}\mathrm{cosec}\,\delta_3 + \frac{1}{R_2}(\cot\delta_2 + \cot\delta_3)\right.$ $+\ \frac{1}{R_3}\sin\varphi_3\,\mathrm{cosec}^3\alpha_3\,\mathrm{cosec}\,\delta_3\left\{\frac{1}{r_4}\sin^2\alpha_3 + \left(\frac{1}{R_3}+\frac{1}{R_2}\right)\sin\varphi_3\sin\alpha_3\right\}\Big]$
τ_2	γ_5	$-\frac{1}{R^2_1}\sin^2\varphi_2\,\mathrm{cosec}^2\alpha_2\,\mathrm{cosec}\,\delta_2$	$\frac{1}{R_2R_3}\sin^2\varphi_2\,\mathrm{cosec}^2\alpha_2\,\mathrm{cosec}\,\delta_3$
τ_3	γ_2		$\Big[\frac{1}{R_2}\sin\varphi_2\,\mathrm{cosec}^3\alpha_2\,\mathrm{cosec}\,\delta_3\left\{\frac{1}{r_2}\sin^2\alpha_2 + \left(\frac{1}{R_1}+\frac{1}{R_2}\right)\sin\alpha_2\sin\varphi_2\right\}\Big]$ $+\ \frac{1}{R_2}\sin^2\varphi_2\,\mathrm{cosec}^2\alpha_2\left(\frac{1}{R_2}\mathrm{cosec}\,\delta_3 + \frac{2}{R_3}\cot\delta_3\right)\Big]$
τ_3	γ_4		$\Big[\frac{1}{R_3}\sin^2\varphi_3\,\mathrm{cosec}^2\alpha_3\left(\frac{1}{R_2}\mathrm{cosec}\,\delta_3 + \frac{2}{R_3}\cot\delta_3\right)$ $+\ \sin\varphi_3\,\mathrm{cosec}^3\alpha_3\left(\frac{1}{R_2}\mathrm{cosec}\,\delta_3 + \frac{2}{R_3}\cot\delta_3\right)\left\{\frac{1}{r_4}\sin^2\alpha_3 + \right.$ $\left.\left(\frac{1}{R_2}+\frac{1}{R_3}\right)\sin\varphi_3\sin\alpha_3\right\} + \frac{1}{R^2_2}\sin^2\varphi_3\,\mathrm{cosec}^2\alpha_3\,\mathrm{cosec}\,\delta_3\Big]$
τ_3	γ_5		$-\Big[\frac{1}{R_2}\sin^2\varphi_2\,\mathrm{cosec}^2\alpha_2\left(\frac{1}{R_2}\mathrm{cosec}\,\delta_3 + \frac{2}{R_3}\cot\delta_3\right) +$ $\frac{1}{R_2}\sin\varphi_2\,\mathrm{cosec}^3\alpha_2\,\mathrm{cosec}\,\delta_3\left\{\frac{1}{r_5}\sin^2\alpha_2 + \left(\frac{1}{R_2}+\frac{1}{R_1}\right)\sin\varphi_2\sin\alpha_2\right\}\Big]$

TABLE C (*contd.*)

3

Coordinates k	k'	μ_X	μ_C
τ_4	γ_1	$-\frac{1}{R_1}\sin\varphi_1\operatorname{cosec}^3\alpha_1\operatorname{cosec}\delta_2\left(\frac{1}{r_1}\sin^2\alpha_1+\frac{2}{R_1}\sin\alpha_1\sin\varphi_1\right)$	$-\left[\frac{1}{R_1}\sin^2\varphi_1\operatorname{cosec}^2\alpha_1\left\{\frac{1}{R_1}\operatorname{cosec}\delta_2+\frac{1}{R_2}(\cot\delta_2-\cot\delta_3)\right\}\right]$
τ_4	γ_2	$\frac{1}{R_1^2}\sin^2\varphi_2\operatorname{cosec}^2\alpha_2\operatorname{cosec}\delta_2$	$-\frac{1}{R_2R_3}\sin^2\varphi_2\operatorname{cosec}^2\alpha_2\operatorname{cosec}\delta_3$
τ_4	γ_3		$\left[\frac{1}{R_3}\sin\varphi_3\operatorname{cosec}^3\alpha_3\operatorname{cosec}\delta_3\left\{\frac{1}{r_3}\sin^2\alpha_3+\left(\frac{1}{R_2}+\frac{1}{R_3}\right)\sin\varphi_3\sin\alpha_3\right\}\right.$ $\left.-\frac{1}{R_3}\sin^2\varphi_3\operatorname{cosec}^2\alpha_3\left\{\frac{1}{R_3}\operatorname{cosec}\delta_3+\frac{1}{R_2}(\cot\delta_2-\cot\delta_3)\right\}\right]$
τ_4	γ_5	$\frac{1}{R_1^2}\sin^2\varphi_2\operatorname{cosec}^2\alpha_2\operatorname{cosec}\delta_2$	$\left[\frac{1}{R_2}\sin^2\varphi_2\operatorname{cosec}^2\varphi_2\left\{\frac{1}{R_3}\operatorname{cosec}\delta_3+\frac{1}{R_2}(\cot\delta_2+\cot\delta_3)\right\}+\right.$ $\sin\varphi_2\operatorname{cosec}^3\alpha_2\left\{\frac{1}{R_1}\operatorname{cosec}\delta_2-\frac{1}{R_2}(\cot\delta_2-\cot\delta_3)\right\}$ $\left.\left\{\frac{1}{r_5}\sin^2\alpha_2+\left(\frac{1}{R_2}-\frac{1}{R_1}\right)\sin\varphi_2\sin\alpha_2\right\}\right]$
τ_5	γ_1	$\frac{1}{R_1}\sin\varphi_1\operatorname{cosec}^3\alpha_1(\operatorname{cosec}\delta_1+\cot\delta_1+\cot\delta_2)$ $\left(\frac{1}{r_1}\sin^2\alpha_1+\frac{2}{R_1}\sin\alpha_1\sin\varphi_1\right)$	$\left[\frac{1}{R_1^2}\sin^2\varphi_1\operatorname{cosec}^2\alpha_1\operatorname{cosec}\delta_1-\frac{1}{R_1}\sin^2\varphi_1\operatorname{cosec}^2\alpha_1\right.$ $\left.\left\{\frac{1}{R_2}\operatorname{cosec}\delta_2(\cot\delta_1-\cot\delta_2)\right\}\right]$
τ_5	γ_2	$-\frac{1}{R_1^2}\sin^2\varphi_2\operatorname{cosec}^2\alpha_2(\operatorname{cosec}\delta_1+\cot\delta_1-\cot\delta_2)$	$-\left[\frac{1}{R_1}\sin\varphi_2\operatorname{cosec}^3\alpha_2\operatorname{cosec}\delta_1\left\{\frac{1}{r_2}\sin^2\alpha_2+\left(\frac{1}{R_1}+\frac{1}{R_2}\right)\sin\varphi_2\sin\alpha_2\right]\right\}$

TABLE C (*contd.*)

Coordinates k	k'	μ_X	μ_C
τ_3	γ_3		$\left[\frac{1}{R_2R_1}\sin^2\varphi_3\operatorname{cosec}^2\alpha_3\operatorname{cosec}\delta_1-\frac{1}{R_2R_3}\sin^2\varphi_3\operatorname{cosec}^2\alpha_3\operatorname{cosec}\delta_2\right]$
τ_5	γ_4		$\left[\frac{1}{R_2}\sin\varphi_3\operatorname{cosec}^3\alpha_3\operatorname{cosec}\delta_2\left\{\frac{1}{r_4}\sin^2\alpha_3-\left(\frac{1}{R_2}-\frac{1}{R_3}\right)\sin\varphi_3\sin\alpha_3\right\}+\frac{1}{R_2}\sin^2\varphi_3\operatorname{cosec}^2\alpha_3\left[\frac{1}{R_2}\operatorname{cosec}\delta_2+\frac{1}{R_1}(\cot\delta_1+\cot\delta_2)\right\}\right]$
τ_1	γ_1'	$-\frac{1}{R_1}(\operatorname{cosec}\delta_1+\cot\delta_1+\cot\delta_2)\sin\varphi_1'\operatorname{cosec}^3\alpha_1\left(\frac{1}{r_1'}\sin^2\alpha_1+\frac{2}{R_1}\sin\varphi_1'\sin\alpha_1\right)$	$-\left[\frac{1}{R_1}\sin^2\varphi_1'\operatorname{cosec}^2\alpha_1\left\{\frac{1}{R_2}\operatorname{cosec}\delta_2+\frac{1}{R_1}(\cot\delta_1-\cot\delta_2)\right\}+\frac{1}{R_1^2}\sin^2\varphi_1'\operatorname{cosec}^2\alpha_1\operatorname{cosec}\delta_1\right.$
τ_2	γ_1'	$\frac{1}{R_1}\sin\varphi_1'\operatorname{cosec}^3\alpha_1\operatorname{cosec}\delta_2\left(\frac{1}{r_1'}\sin^2\alpha_1+\frac{2}{R_1}\sin\varphi_1'\sin\alpha_1\right)$	$\left[\frac{1}{R_1}\sin^2\varphi_1'\operatorname{cosec}^2\alpha_1\left\{\frac{1}{R_1}\operatorname{cosec}\delta_2-\frac{1}{R_2}(\cot\delta_2+\cot\delta_3)\right\}\right]$
τ_4	γ_1'	$-\frac{1}{R_1}\sin\varphi_1'\operatorname{cosec}^3\alpha_1\operatorname{cosec}\delta_2\left(\frac{1}{r_1'}\sin^2\alpha_1+\frac{2}{R_1}\sin\varphi_1\sin\alpha_1\right)$	$-\left[\frac{1}{R_1}\sin^2\varphi_1'\operatorname{cosec}^2\alpha_1\left\{\frac{1}{R_1}\operatorname{cosec}\delta_2+\frac{1}{R_2}(\cot\delta_2+\cot\delta_3)\right\}\right]$
τ_5	γ_1'	$\frac{1}{R_1}\sin\varphi_1'\operatorname{cosec}^3\alpha_1(\operatorname{cosec}\delta_1+\cot\delta_1+\cot\delta_2)\left(\frac{1}{r_1'}\sin^2\alpha_1+\frac{2}{R_1}\sin\varphi_1'\sin\alpha_1\right)$	$\left[\frac{1}{R_1^2}\sin^2\varphi_1'\operatorname{cosec}^2\alpha_1\operatorname{cosec}\delta_1-\frac{1}{R_1}\sin^2\varphi_1'\operatorname{cosec}^2\alpha_1\left\{\frac{1}{R_2}\operatorname{cosec}\delta_2+\frac{1}{R_1}(\cot\delta_2+\cot\delta_1)\right\}\right]$
		$g_{\tau_3\gamma_1'}=g_{\tau_3,\gamma_1}=0$	$g_{kk'}=g_{k'k}$

The significance of various symbols can be found in the text. The applicability of these with regard to the substituted Furans, thiophenes, and pyrroles is mentioned in the text i.e., subjected to the statements 5......9 stated therein.

As all the ring angles are found to be obtuse for the above molecules, the supplementary values of the α's are introduced and denoted by δ with the proper change in sign as regards the trigonometrical expressions.

The expressions are the same for any substituted compound of the above molecules, if,

(*i*) the equilibrium angles and distances are assumed to remain unaltered,

(*ii*) planar structure of the molecule is retained, and

(*iii*) substitution is made on the H atoms. They will hold even if the substitution is made on the H atoms of the (CH_2) group in cyclopentadiene and the H atom of N—H bond in case of pyrrole (figure 2c).

But when substitution is made on the ring atom the general expressions in Table I should be used, as the equilibrium distances and angles are expected to vary.

In Table III are given the *s* vector expressions for the atoms when out-of-plane bending coordinates are considered using the expressions given by Malhiot and Ferigle (1955).

The particular expressions applicable to furan, pyrrole, thiophene and cyclopentadiene are shown separately in Table IV. While reading the Table IV the following points are to be noted ;

1. The expressions under 1st and 6th columns do not arise in case of furan, thiophene and their substitutions as there are no bonds on atom (1) defining γ in the above cases.

2. Column 1 should be used along with the other columns in case of pyrrole and its substitutions. However, column 6 should be omitted in this case also.

3. All the 6 columns should be used for cyclopentadiene and its substitutions where the 1st and the last columns represent the out of plane bending of the two C—H bonds of (CH_2) group.

4. In all the above cases except in cyclopentadiene

$$\phi_1 = W - \frac{\alpha_i}{2} \quad \text{where} \quad i = 1, 2 \text{ and } 3.$$

But in case of cyclopentadiene $\phi_1' = \phi_1 +$ the angle fo med betw en the wo C—H bonds of CH_2 group. And the remaining ϕ's satisfy

$$\phi_i = W - \frac{\alpha_i}{2}$$

where i now stands fo 2 and 3 only (Fig. 2abc).

5. In all the above cases it is seen from the experimental data that $r_1' = r_1$ (equilibrium C—H bond length of CH_2 group in cyclopentadiene) and $r_2 = r_3$

$= r_4 = r_5$ equilibrium C—H bond length in all the molecules. The Table IV is applicable for all the substituted compounds if it is assumed that.

6. The angles of the ring of the substituted compound remain unaltered from those of its parent molecule.

7. The bond distances of the ring in the equilibrium position also remain unaltered for the substituted compounds and

8. The orientation of the bonds remain unaltered for the substituted compounds. Assumptions 6, 7, 8 are considered to be fairly justifiable if the substitutions are made not on the ring but on the H atoms of the parent molecules.

9. The other factors being sati fied, Table IV is applicable even if different substitutions are made on the H atoms. It is for this purpose only r_i's are retained in the Table IV without taking into consideration the statements of 5. (Otherwise Table III should be referred to, which is applicable even if th ring atom is substituted for). In all these tables $\vec{V}$ stands for the unit vector upwards perpendicular to the equilibrium plane of the molecule.

(b) *Inverse kinetic energy matrix elements*

Using Tables II and IV and the equation 1, the elements of the inverse kinetic energy matrix of torsional vibrations, out-of-plane bending vibrations and the interaction between the above two are derived, and are separately given in Tables A, B & C. While reading these tables, the first column represents the pair of the coordinates contributing to the matrix μ_C, μ_H and μ_X, are the reciprocal masses of carbon atom, hydrogen atom and O,N,S or C according as the atom is oxygen, nitrogen, sulphur or carbon. The coefficients of the reciprocal masses are given under the corresponding columns. The absence of expressi n under any column and against any row means that, the particular μ vanishes in the corresponding element g. In order to read a particular $g_{kk'}$, the expressions against that pair of coordinates are to be first multiplied by the corresponding μ's and then finally added up, for example $g_{\gamma_1\gamma_1}$ in Table B $g_{\gamma_1\gamma_1}$ is

$$\mu_H \frac{1}{r_1^2} \sin^2\phi_1 \operatorname{cosec}^2\alpha_1 + \mu_X\left[\sin^2\phi_1 \operatorname{cosec}^6\alpha_1 \left(\frac{1}{r_1}\sin^2\alpha_1 + \frac{2}{R_1}\sin\alpha_1 \sin\phi_1\right)^2\right] + 2\mu_C \frac{\sin^4\phi_1 \operatorname{cosec}^2\alpha_1}{R_1^2}$$

In all these tables it is to be noted that $g_{kk'} = g_{k'k}$. The elements can be directly used to arrive at the (G) matrix elements for the out-of-plane modes of vibrations for furan, pyrrole, thiophene, cyclopentadiene and their substitutions, leading ultimately to values of the out-of-plane valence force constants for these molecules.

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